Alkylation of Isobutane/2-butene over Modified FAU-type Zeolites

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Abstract: A series of mesoporous La-zeolite X catalysts were prepared by a hydrothermal method with a variation of carbon template content. The prepared catalysts were applied to the isobutane/2-butene alkylation. Mesopore volume of the catalysts increased with increasing carbon template content, while acidity of the catalysts decreased with increasing carbon template content. Productivity of C8 alkylate showed volcano-shaped trends with respect to carbon template content. Among the catalysts, La-0.5-Zeol X showed the highest productivity for C8 alkylate. The maximum productivity for C8 alkylate were due to the offset of two opposite trends between mesopore volume and acidity of the catalysts.

Keywords: Isobutane/2-butene alkylation, Zeolite X, Hard templating method.

1. Introduction

Alkylate is one of the most environmentally friendly gasoline raw materials. Alkylate has high octane value and does not contain harmful substances such as olefin, aromatic compound, and sulfur.[1] Alkylate is conventionally produced by isobutane/olefin alkylation processes over acid catalysts. Currently, there are two types of commercial alkylation processes using sulfuric acid and fluoric acid. These alkylation processes have corrosion, safety, and environmental problems because they use toxic and corrosive liquid acids. Therefore, studies on solid acid-catalyzed alkylation have been widely investigated. Among various solid acid catalysts, zeolite is considered to be one of the most suitable solid acid catalysts for this reaction. However, no commercial alkylation process utilizing zeolite has been developed due to the limited catalytic activity of zeolite.

In the alkylation reaction over solid acid catalyst, various side reactions occur. These side reactions produce materials having large molecular weight and size which can be deposited inside the pores of the catalyst, leading to an adverse effect on the mass transfer.[2] It has been reported that hydride transfer of isobutane is favored over zeolites having low Si/Al ratio. It is also known that lanthanum-exchanged zeolites promote hydride transfer of isobutane effectively. Thus, lanthanum-exchanged zeolite X has attracted much attention because of low Si/Al ratio and high concentration of acid sites. However, deactivation by carbon deposition in the catalyst pores still occurs. Therefore, prevention of catalyst deactivation by promotion of mass transfer is essential for commercialization of zeolite-based alkylation process.

2. Experimental

A series of La-x-Zeol X catalysts were prepared by a hydrothermal method with a variation of carbon template content (x, C template / (Si+Al) wt%).

N_2 adsorption-desorption measurements were conducted to measure textural properties of La-x-Zeol X catalysts. Surface areas of the catalysts were determined by the Brunaur-Emmett-Teller (BET) method. Micropore volumes of the catalysts were calculated by the MP (micropore) analysis method, and mesopore volumes of the catalysts was calculated by the Barrett-Joyner-Halenda (BJH) method applied to desorption branch of the N_2 isotherm. Silicon (Si), aluminum (Al), and lanthanum (La) contents in the La-x-Zeol X catalysts were measured by ICP-AES analyses. X-ray diffraction patterns of the catalysts were obtained by XRD. NH_3-TPD analyses were conducted to measure acid property of La-x-Zeol X catalysts

Alkylation of isobutane/2-butene to C8 alkylate was carried out in a batch reactor at 80 °C and 20 bar. The composition of isobutane/2-butene mixture was isobutene : 2-butene = 50 : 1. Reaction products were sampled every 1 h and analyzed with gas chromatograph equipped with a flame ionization detector (HP-

PONA). Various components of products were identified by a mass spectrometer equipped with a capillary column (HP-5).

3. Results and discussion

Textural properties of La-x-Zeol X catalysts were measured by N_2 adsorption-desorption isotherm measurements. It was found that surface area (250.7-303.1 m^2/g) and mesopore volume (0.084-0.238 cm^3/g) increased with increasing carbon template content. This means that mesoporous zeolite X catalysts were successfully prepared by a hard templating method and mesoporosity of the catalysts were successfully controlled by adjusting carbon template content.

NH_3-TPD analyses were conducted to investigate acid property of La-x-Zeol X. Acidity of the catalysts decreased with increasing carbon template content. This is because hard template disturbs development of zeolite acid center during the crystallization process.

As shown in Figure 1, productivity of C8 alkylate and selectivity for C8 alkylate over La-x-Zeol X catalysts showed volcano-shaped trends with respect to carbon template content.

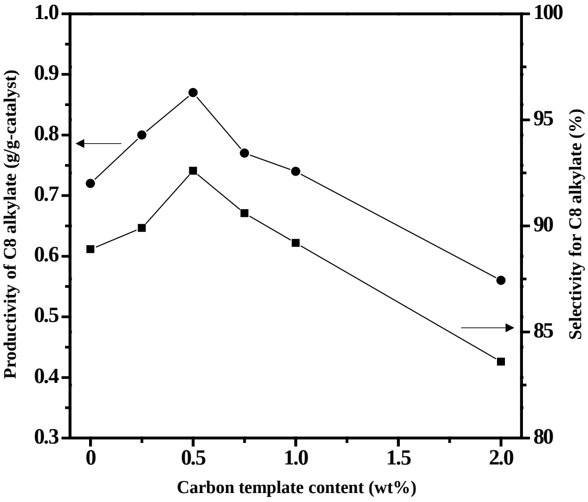

Figure 1. Productivity and selectivity of C8 alkylate with respect to carbon template content.

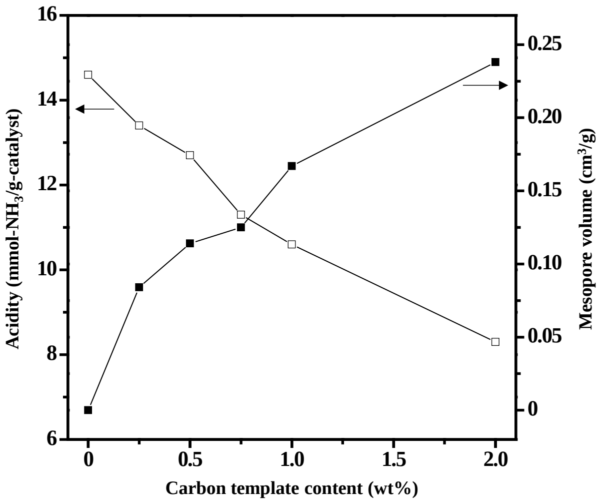

Figure 2. Acidity and mesopore volume of La-x-Zeol X with respect to carbon template content.

In Figure 2, mesopore volume and acidity of La-x-Zeol X catalysts are plotted with respect to carbon template content. It was found that mesopore volume of the catalysts increased with increasing carbon template content while acidity of the catalysts decreased with increasing carbon template content. It is reported that high molecular weight products deposited in the pores of zeolite disturb mass transfer of reactants and products.[3]

4. Conclusions

Well-developed mesoporosity of the catalysts gives a positive effect on the catalytic performance due to the enhanced mass transfer of high molecular weight products. However, small acidity gives a negative effect on the catalytic performance because small acidity retards the mobility of proton in isobutane and the hydrogen exchange step of alkylation reaction. In conclusion, these two opposite effects of mesopore volume and acidity gave rise to the volcano-shaped trends of C8 alkylate productivity and C8 alkylate selectivity with respect to carbon template content.

References

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